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PCT**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P28791PC00	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/ZA 03/00188	International filing date (day/month/year) 19.12.2003	Priority date (day/month/year) 20.12.2002
International Patent Classification (IPC) or both national classification and IPC B01J31/18		
Applicant SASOL TECHNOLOGY (PTY) LIMITED et al.		



1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 17 sheets.

3. This report contains indications relating to the following items:

I	<input checked="" type="checkbox"/>	Basis of the opinion
II	<input type="checkbox"/>	Priority
III	<input type="checkbox"/>	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	<input type="checkbox"/>	Lack of unity of invention
V	<input checked="" type="checkbox"/>	Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	<input type="checkbox"/>	Certain documents cited
VII	<input checked="" type="checkbox"/>	Certain defects in the international application
VIII	<input type="checkbox"/>	Certain observations on the international application

Date of submission of the demand 18.05.2004	Date of completion of this report 07.04.2005
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Thomas, D Telephone No. +49 89 2399-7837 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/ZA 03/00188

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-15, 18 as originally filed
16, 17, 19-22 filed with telefax on 10.11.2004

Claims, Numbers

1-47 filed with telefax on 16.02.2005

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

see separate sheet

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6. Additional observations, if necessary:

see separate sheet

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-47
	No: Claims	
Inventive step (IS)	Yes: Claims	1-47
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-47
	No: Claims	

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

A reasonable statement concerning novelty and inventive step is at the present stage not possible (Problems with Article 6 PCT, s next paragraph)

Certain defects in the international application

Present claim 1 describes a process for the polymerization of olefines.
The heteroatomic ligand used in said process is described by a markush formula with R¹-R⁴ being a hydrocarbyl or heterohydrocarbyl groups.
The substitution pattern of R¹-R⁴ is further restricted, but a clear definition of what is regarded to be the hydrocarbyl or heterohydrocarbyl group and what is regarded to be a substituent is missing.

(Where does the heterohydrocarbyl group end and where does the substituent start ? example: R¹ = (MeO)Ph or R¹ = Ph and Substituent = OMe ?

s. claim 18 and condition (I) of claim 1: any substituents on R¹-R⁴ are not electron donating)

Re Item VII.

Present claim 1 does not meet requirements of Article 41(2).
Claim 1 describes under (ii) a heteroatomic ligand with the formula:
(R¹)(R²)A-B-C(R³)(R⁴) with

A,C are independently selected from P,As,Sb, Bi and N

B is a linking group between A and C

a) wherein at least one of R¹,R²,R³ and R⁴ is substituted with a polar substituent on a second or further atom from the atom bound to A

b) and any polar substituents on R¹,R²,R³ and R⁴ are not on the atom adjacent to

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the atom bond to A or C.

Basis for a) , b) can be found on page 7, line 6-9. Page 7 does not teach or disclose to combine feature a) with b) . Basis for claim 1 can therefore not be derived from the description.

The old set of claims discloses features A (claim 10) and B (claim 12) as well.

The combination of preferred embodiments (claims) does not add subject matter to the application as originally filed.

Both claims refer back to claim 9 which specifies that R^1 - R^4 are aromatic including heteroaromatic groups. The old set of claims therefore only disclose a heteroatomic ligand with the formula:

$(R^1)(R^2)A-B-C(R^3)(R^4)$ with

A,C are independently selected from P,As,Sb, Bi and N

B is a linking group between A and C

a) wherein at least one of R^1 , R^2 , R^3 and R^4 is substituted with a polar substituent on a second or further atom from the atom bound to A

b) and any polar substituents on R^1 , R^2 , R^3 and R^4 are not on the atom adjacent to the atom bond to A or C.

c) and R^1 - R^4 are aromatic including heteroaromatic groups

The amendments filed with the telefax dated 16.02.2005 introduce therefore subject-matter which extends beyond the content of the application as filed, contrary to Article 34(2)(b) PCT.

According to yet another aspect of the invention the tetramerisation process includes the step of contacting an olefinic feedstream with a catalyst system which includes a transition metal and a heteroatomic ligand and wherein the product of the tetramerisation process is an olefin and the olefin is concomitantly copolymerised with the olefinic feedstream by contacting the olefins produced in the first step and the olefinic feedstream with a catalyst comprising of a transition metal and/or a homo- or heteroatomic ligand.

By homoatomic is meant a ligand that consists entirely of similar atoms such as carbon that constitute the skeleton of the ligand such as the cyclopentadienyl ligand for example.

The ethylene to be tetramerised and polymerised can be introduced into the process according to the invention in a continuous or batch fashion.

The tandem catalysis product stream will be understood to include a polymer, which polymer is produced according to the invention in a continuous or batch fashion.

The process may include a process for tetramerisation of ethylene to selectively yield 1-octene.

The process may be a process for tetramerisation of ethylene and concomitant polymerisation of the produced 1-octene with ethylene.

The ethylene may be contacted with the catalyst system comprising of the tetramerisation catalyst and the polymerisation catalyst at a pressure of 100 kPa (1 barg), preferably greater than 1000 kPa (10 barg), more preferably greater than 3000 kPa (30 barg).

The tandem catalysis process may include the step of mixing the components of the catalyst systems (both the tetramerisation catalyst and the polymerisation catalyst) at any temperature between -20°C and 250°C in the presence of an olefin. The preferred temperature range being 20°C - 100 °C.

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The individual components of both catalyst systems described herein may be combined simultaneously or sequentially in any order, and in the presence or absence of a solvent in order to give active catalysts. The presence of an olefin during the mixing of the catalyst components generally provides a protective effect which may result in improved catalyst performance. The preferred temperature range may be between 20°C and 100°C.

The reaction products derived from the tandem catalysis process as described herein may be prepared using the disclosed catalyst system by a homogeneous liquid phase reaction in the presence or absence of an inert solvent, and/or by slurry reaction where the catalyst system is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which neat reagent and/or product olefins serve as the dominant medium, and/or gas phase reaction using conventional equipment and contacting techniques.

The tandem catalysis process may also be carried out in an inert solvent. Any inert solvent that does not react with the activator can be used. These inert solvents may include saturated aliphatic, unsaturated aliphatic, aromatic hydrocarbon and halogenated hydrocarbon. Typical solvents include, but are not limited to, benzene, toluene, xylene, cumene, heptane, methylcyclohexane, methylcyclopentane, cyclohexane, ionic liquids and the like.

The tandem catalysis process may be carried out at pressures from atmospheric to 50000 kPa (500 barg). Ethylene pressures in the range of 1000-7000 kPa (10-70 barg) are preferred. Particularly preferred pressures range from 3000-5000 kPa (30-50 barg).

The tandem catalysis process may be carried out at temperatures from -20 °C - 250 °C. Temperatures in the range of 15-130 °C are preferred. Particularly preferred temperatures range from 35-150°C.

The tandem catalysis process may be carried out in a plant which includes any type of reactor. Examples of such reactors include, but are not limited to, batch reactors, semi-batch reactors and continuous reactors. The plant may include, in combination, a) a reactor, b) at least one inlet line into this reactor for olefin reactant and the catalyst

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A solution of 9.8 mg of $(p\text{-methoxyphenyl})_2\text{PN}(\text{isopropyl})\text{P}(p\text{-methoxyphenyl})_2$ (0.018 mmol) in 10 ml of toluene was added to a solution of 5.8 mg $\text{CrCl}_3(\text{THF})_3$ (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80 ml) and MAO (methylaluminoxane, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.0831 g of polyethylene. The GC analyses indicated that the reaction mixture contained 42.72 g oligomers. The oligomers comprised 72% 1-octene (99% purity).

Example 2: Ethylene tetramerisation reaction using $\text{Cr}(\text{acetylacetonate})_3$, $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$ and MAO

A solution of 18.8 mg of $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$ (0.044 mmol) in 6.4 ml of cumene was added to a solution of 7.7 mg $\text{Cr}(\text{acetylacetonate})_3$ (0.022 mmol) in 8 ml cumene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 1000 ml pressure reactor (autoclave) containing a mixture of cumene (180 ml) and MAO (methylaluminoxane, 4.4 mmol, 10 % solution in toluene) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 25 min; and the procedure of Example 2 above was employed. The product mass was 118.78 g. The product comprised 69.5% 1-octene (98.9% purity).

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Example 3: Tandem catalysis reaction using $\text{Cr}(\text{acetylacetonate})_3$, $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$, MAO and dimethylsilyl-bis(2-methyl(4,5)benzoindenyl) zirconium dichloride.

In this example, 0.011 mmol Chromium acetylacetonate (15.2 mg) was combined with 0.022 mmol $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$ (36 mg) in a Schlenk tube under an argon atmosphere with 10 ml anhydrous toluene as solvent. The metal salt and the ligand was stirred for 5 minutes and then added under inert conditions to a Parr autoclave (300 ml capacity). The autoclave was filled *a priori* with 70 ml anhydrous toluene as solvent. Separately, 2 ml of a solution of dimethylsilyl-bis(2-methyl(4,5)benzoindenyl) zirconium dichloride (0.0052 mmol, 0.0022 mg) was added to 18 ml anhydrous toluene in a separate reservoir under inert conditions connected to the inlet of an HPLC pump. Approximately 1200 eq. (on Cr) methylaluminoxane (MAO) was added to the autoclave under argon atmosphere. The autoclave was heated to 45 °C, sealed and pressurised to 3500 kPa (35 barg) with ethylene whilst stirring was commenced at 1200 rpm. At the same time the polymerisation catalyst solution was added to the autoclave through an inlet on the Parr reactor that was connected to the outlet of the HPLC pump. The polymerisation catalyst was added at a rate of 0.66 ml/min over a period of 30 minutes after which the reaction vessel was cooled down and quenched with ethanol. After 30 minutes, the autoclave was opened and the contents collected for analysis. The amount of polymer collected was found to be 23.16 g with a melting point of 126 °C and an amount of 1-octene incorporation as determined by ^{13}C nuclear magnetic resonance spectroscopy of 3.83 %.

Example 4: Tandem catalysis reaction using $\text{Cr}(\text{acetylacetonate})_3$, $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$, MAO and tetramethylcyclopentadienyl dimethylsilyl t-butylamidate titanium dichloride.

In this example, a solution of 20 ml $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$ (0.044 mmol) in anhydrous toluene and 20 ml of a solution of $\text{Cr}(\text{acetylacetonate})_3$ (0.022 mmol) in 30 ml

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anhydrous toluene was added to a Parr autoclave (300 ml capacity). At the same time 10 ml of a solution of tetramethylcyclopentadienyl-dimethylsilyl-t-butylamido- titanium dichloride (0.026 mmol, 0.01 mg) was added to an external reservoir along with 10 ml anhydrous toluene. The external reservoir (under argon atmosphere) was connected to the inlet of an HPLC pump. Approximately 1200 eq (on Cr) methylaluminoxane (MAO) was added to the autoclave under inert conditions. The autoclave was heated to 45 °C, sealed and pressurised to 4300 kPa (43 barg) with ethylene whilst stirring was commenced at 1200 rpm. At the same time the polymerisation catalyst solution was added to the autoclave through a separate inlet on the Parr reactor that was connected to the outlet of the HPLC pump. The polymerisation catalyst was added at a rate of 0.66 ml/min over a period of 30 minutes after which the reaction vessel was cooled down and quenched with ethanol. The autoclave was opened and the contents collected for analysis. Analysis of the polymer after drying in vacuum for 12 h at 60 °C revealed a melting point of 99 °C and 2.39 % incorporation of 1-octene as determined using ¹³C NMR. The amount of polymer collected was 24.53g. The density of the polymer was determined to be 0.9202 g.cm⁻³.

Example 5: Tandem catalysis reaction using (p-methoxyphenyl)₂PN(isopropyl)P(p-methoxyphenyl)₂, Cr(acetylacetonate)₃, MAO and dimethylsilyl bisindenyl zirconium dichloride

In this example, 10 ml of a toluene solution containing 0.03 mmol chromium acetylacetonate was combined with 0.06 mmol (p-methoxyphenyl)₂PN(isopropyl)P(p-methoxyphenyl)₂ [30 mg] in a Schlenk tube under an argon atmosphere. The metal salt and the ligand was stirred for 5 minutes and then added to a Parr autoclave (300 ml capacity) under inert conditions. The autoclave was filled *a priori* with 60 ml anhydrous toluene as solvent. Separately, 5 ml of a solution of dimethylsilyl bisindenyl zirconium dichloride (0.015 mmol, 0.0067 mg), was added to 15 ml anhydrous toluene in a separate reservoir under argon that was connected to the inlet of an HPLC pump. Approximately 600 eq (on Cr) methylaluminoxane (MAO) was added to the autoclave under inert conditions. The autoclave was heated to 45 °C, sealed and pressurised to a pressure of 4100 kPa (41 barg) with ethylene whilst stirring was commenced at 1200 rpm. At the same time the polymerisation catalyst solution was added to the autoclave through a separate inlet connected to the outlet of the HPLC pump. The polymerisation catalyst

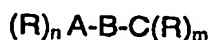
was added at a rate of 0.33 ml/min over a period of 60 minutes after which the reaction vessel was cooled down and quenched with ethanol. The autoclave was opened and the contents collected for analysis. The amount of polymer collected was first dried in a vacuum oven at 60 °C for 12 h yielding an amount of 51.1 g with a melting point of 106 °C and an amount of 1-octene incorporated as determined by ¹³C nuclear magnetic resonance spectroscopy of 5.55 %. The density of the polymer was determined to be 0.8155 g.cm⁻³.

Example 6: Tandem catalysis reaction using (p-methoxyphenyl)₂-PN(isopropyl)P(p-methoxyphenyl)₂, Cr(acetylacetonate)₃, MAO and cyclopentadienyl dimethylsilyl titanium dichloride

In this example, 0.025 g of (p-methoxyphenyl)₂-PN(isopropyl)P(p-methoxyphenyl)₂ (0.06 mmol) was added to 10 ml of a toluene solution of Cr(acetylacetonate)₃ (0.03 mmol) in a Schlenk tube under an argon atmosphere and allowed to stir for 5 minutes until fully dissolved. At the same time, 10 ml of a cyclopentadienyl dimethylsilyl titanium dichloride (0.03 mmol, 0.009 mg) solution in toluene was added to an external reservoir along with 10 ml anhydrous toluene. The external reservoir was connected to the inlet of an HPLC pump. After this, the 300 ml Parr autoclave was charged with 60 ml anhydrous toluene as well as the previously stirred Cr(acetylacetonate)₃/(p-methoxyphenyl)₂-PN(isopropyl)P(p-methoxyphenyl)₂ ligand solution under inert conditions. Approximately 600 eq (on Cr) methylaluminoxane (MAO) was added to the autoclave under inert conditions. The autoclave was connected to the HPLC pump outlet and heated to 45 °C, sealed and pressurised to a pressure of 5300 kPa (53 barg) with ethylene for the duration of the reaction (60 minutes) whilst stirring was commenced at 1200 rpm. At the same time the polymerisation catalyst solution was added to the autoclave through the HPLC pump. The polymerisation catalyst was added at a rate of 0.33 ml/min over a period of 60 minutes after which the reaction vessel was cooled down and quenched with ethanol. The autoclave was opened and the contents collected for analysis. The polymer collected was washed in acetone and dried in a vacuum oven for 12h at 60 °C. The dried polymer amounted to 3.35 g. Analyses of the polymer revealed a melting point of 128 °C and 1.02 % incorporation of 1-octene as determined by ¹³C NMR.

1. A process for polymerising olefins to branched polyolefins by contacting at least one olefin with a combination of catalysts comprising

- (a) a polymerisation catalyst; and
- (b) at least one co-catalyst in the form of an ethylene tetramerisation catalyst to produce 1-octene from ethylene which co-catalyst includes the combination of
 - a transition metal compound; and
 - a heteroatomic ligand described by the general formula



wherein

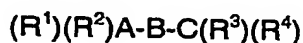
A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium and nitrogen;

B is a linking group between A and C;

the R groups are the same or different, and each R is independently selected from any homo or hetero hydrocarbyl group; and

n and m for each R is independently determined by the respective valence and oxidation state of A and C; and

provided that where the heteroatomic ligand is described by the following general formula



wherein

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen;

B is a linking group between A and C; and

R^1 , R^2 , R^3 and R^4 are independently selected from the group consisting of a hydrocarbyl group, a heterohydrocarbyl group, a substituted hydrocarbyl group and a substituted heterohydrocarbyl group; R^1 , R^2 , R^3 and R^4 being characterised therein that either

- (i) any substituents on one or more of R^1 , R^2 , R^3 and R^4 are not electron-donating; and where R^1 , R^2 , R^3 and R^4 are independently aromatic, including heteroaromatic groups, not all the groups R^1 ,

- R^2 , R^3 and R^4 have a substituent on the atom adjacent to the atom bound to A or C; or
- (ii) at least one of R^1 , R^2 , R^3 and R^4 is substituted with a polar substituent on a second or further atom from the atom bound to A or C and provided that any polar substituents on R^1 , R^2 , R^3 and R^4 are not on the atom adjacent to the atom bound to A or C.
2. The process as claimed in claim 1 wherein the olefin is ethylene and the branched polyolefin is a branched polyethylene.
3. The process as claimed in claim 1 or claim 2 wherein the branched polyolefin is linear low density polyethylene.
4. The process as claimed in any one of the preceding claims, wherein the heteroatomic ligand of the co-catalyst is described by the general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth, and nitrogen; B is a linking group between A and C; and R^1 to R^4 are independently selected from the group consisting of a hydrocarbyl group, a heterohydrocarbyl group, and a substituted heterohydrocarbyl group, R^1 to R^4 being characterised therein that either
- (i) any substituents on one or more of R^1 , R^2 , R^3 and R^4 are not electron-donating; and where R^1 , R^2 , R^3 and R^4 are independently aromatic, including heteroaromatic groups, not all the groups R^1 , R^2 , R^3 and R^4 have a substituent on the atom adjacent to the atom bound to A or C; or
- (ii) at least one of R^1 , R^2 , R^3 and R^4 is substituted with a polar substituent on a second or further atom from the atom bound to A or C and provided that any polar substituents on R^1 , R^2 , R^3 and R^4 are not on the atom adjacent to the atom bound to A or C.
5. The process as claimed in claim 4 wherein R^1 , R^2 , R^3 and R^4 are independently selected from the group consisting of a non-aromatic group, and an aromatic group, including a heteroaromatic group.

6. The process as claimed in claim 5 wherein each of R^1 , R^2 , R^3 and R^4 is independently an aromatic, including a heteroaromatic group and not all the groups R^1 , R^2 , R^3 and R^4 have a substituent on the atom adjacent to the atom bound to A or C.
7. The process as claimed in claim 6 wherein not more than two of R^1 , R^2 , R^3 and R^4 have substituents on the atom adjacent to the atom bound to A or C.
8. The process as claimed in any one of claims 4 to 7 wherein any polar substituent on one or more of R^1 , R^2 , R^3 and R^4 is electron-donating.
9. The process as claimed in any one of claims 4 to 7 wherein each non-electron donating substituent is non-polar.
10. The process as claimed in any one of claims 1 to 9 wherein B is selected from the group consisting of an organic linking group comprising a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl; an inorganic linking group comprising a single atom linking spacer; and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, $-B(R^5)-$, $-Si(R^5)_2-$, $-P(R^5)-$ and $-N(R^5)-$ where R^5 is selected from the group consisting of hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom, a halogen, a cyclic heteroatomic group or a cyclic homoatomic group.
11. The process as claimed in claim 10 wherein B is a single atom linking spacer.
12. The process as claimed in claim 10, wherein B is $-N(R^5)-$, wherein R^5 is hydrogen or selected from the group consisting of alkyl, aryl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, aryl substituted with any of these substituents, and any cyclic heteroatomic group including cyclopentadienyl dimethylsilyl-t-butylamidato or a cyclic homoatomic group including cyclopentadienyl, indenyl and fluorene.
13. The process as claimed in any one of claims 1 to 12, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.

14. The process as claimed in any one of claims 1 to 12, wherein A and/or C is independently phosphorus.
15. The process as claimed in claim 4, wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group consisting of a benzyl, phenyl, tolyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl, thiophenoxy, trimethylsilyl, dimethylhydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and a tetrahydrofuranyl group.
16. The process as claimed in claim 4 wherein R^1 , R^2 , R^3 and R^4 are independently selected from the group consisting of a phenyl, tolyl, biphenyl, naphthyl, thiophenyl and ethyl group.
17. The process as claimed in claim 1 or claim 4, wherein the heteroatomic ligand is selected from the group consisting of
- (phenyl)₂PN(methyl)P(phenyl)₂, (phenyl)₂PN(pentyl)P(phenyl)₂,
 - (phenyl)₂PN(phenyl)P(phenyl)₂, (phenyl)₂PN(p-methoxyphenyl)P(phenyl)₂,
 - (phenyl)₂PN(p-butylphenyl)P(phenyl)₂, (phenyl)₂PN((CH₂)₃-N-morpholine)P(phenyl)₂,
 - (phenyl)₂PN(Si(CH₃)₃)P(phenyl)₂,
 - ((phenyl)₂P)₂NCH₂CH₂)₃N, (ethyl)₂PN(methyl)P(ethyl)₂,
 - (ethyl)₂PN(isopropyl)P(phenyl)₂, (ethyl)(phenyl)PN(methyl)P(ethyl)(phenyl),
 - (ethyl)(phenyl)PN(isopropyl)P(phenyl)₂,
 - (phenyl)₂P(=Se)N(isopropyl)P(phenyl)₂, (phenyl)₂PCH₂CH₂P(phenyl)₂, (o-ethylphenyl)(phenyl)PN(isopropyl)P(phenyl)₂,
 - (o-methylphenyl)₂PN(isopropyl)P(o-methylphenyl)(phenyl), (phenyl)₂PN(benzyl)-P(phenyl)₂,
 - (phenyl)₂PN(1-cyclohexylethyl)P(phenyl)₂,
 - (phenyl)₂PN[CH₂CH₂CH₂Si(OMe)₃]P(phenyl)₂,
 - (phenyl)₂PN(cyclohexyl)P(phenyl)₂, (phenyl)₂PN(2-methylcyclohexyl)P(phenyl)₂,
 - (phenyl)₂PN(allyl)P(phenyl)₂, (o-naphthyl)₂PN(methyl)P(o-naphthyl)₂,
 - (p-biphenyl)₂PN(methyl)P(p-biphenyl)₂,
 - (p-Me-phenyl)₂PN(methyl)P(p-Me-phenyl)₂, (o-thiophenyl)₂PN(methyl)P(o-thiophenyl)₂,
 - (phenyl)₂PN(methyl)N(methyl)P(phenyl)₂, (m-Me-phenyl)₂PN(methyl)P(m-Me-phenyl)₂,
 - (phenyl)₂PN(isopropyl)P(phenyl)₂,

(phenyl)₂P(=S)N(isopropyl)P(phenyl)₂ and
 (phenyl)₂P(=S)N(isopropyl)P(=S)(phenyl)₂

18. The process as claimed in claim 1 or 4, wherein the heteroatomic ligand is selected from the group consisting of ((*m*-methoxyphenyl)₂PN(methyl)P(*m*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(methyl)P(*p*-methoxyphenyl)₂, (*m*-methoxyphenyl)₂PN(isopropyl)P(*m*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(isopropyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(2-ethylhexyl)P(*p*-methoxyphenyl)₂, (*m*-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂ and (*p*-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂, (*m*-methoxyphenyl)(phenyl)PN(methyl)P(*m*-methoxyphenyl)(phenyl), (*p*-methoxyphenyl)(phenyl)PN(methyl)P(*p*-methoxyphenyl)(phenyl), (*m*-methoxyphenyl)₂PN(methyl)P(phenyl)₂ and (*p*-methoxyphenyl)₂PN(methyl)P(phenyl)₂, (*p*-methoxyphenyl)₂PN(1-cyclohexylethyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(2-methylcyclohexyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(decyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(pentyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(benzyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(phenyl)P(*p*-methoxyphenyl)₂, (*p*-fluorophenyl)₂PN(methyl)P(*p*-fluorophenyl)₂, (*o*-fluorophenyl)₂PN(methyl)P(*o*-fluorophenyl)₂, (*p*-dimethylamino-phenyl)₂PN(methyl)P(*p*-dimethylamino-phenyl)₂, (*p*-methoxyphenyl)₂PN(allyl)P(*p*-methoxyphenyl)₂, (*p*-(*p*-methoxyphenyl)-phenyl)₂PN(isopropyl)P(*p*-(*p*-methoxyphenyl)-phenyl)₂ and (*p*-methoxyphenyl)(phenyl)PN(isopropyl)P(phenyl)₂.
19. The process as claimed in any one of the preceding claims wherein the polymerisation catalyst is selected from the group consisting of a Ziegler-Natta catalyst, an unbridged metallocene, a half sandwich metallocene, a carbon-bridged metallocene and a silyl-bridged metallocene.
20. The process as claimed in claim 19, wherein the Ziegler-Natta catalyst is selected from the group consisting of TiCl₃-Et₂AlCl, AlR₃-TiCl₄.
21. The process as claimed in claim 19, wherein the unbridged metallocene is selected from the group consisting of:
 bis(cyclopentadienyl)chromium(II),

bis(cyclopentadienyl)-zirconium Chloride hydride,
bis(cyclopentadienyl)-titanium dichloride,
bis(cyclopentadienyl)-zirconium dichloride,
bis(cyclopentadienyl)-zirconium dimethyl,
bis(*n*-butylcyclopentadienyl)-zirconium dichloride,
bis(*n*-dodecylcyclopentadienyl)-zirconium dichloride,
bis(ethylcyclopentadienyl)-zirconium dichloride,
bis(iso-butylcyclopentadienyl)-zirconium dichloride,
bis(isopropylcyclopentadienyl)-zirconium dichloride,
bis(methylcyclopentadienyl)-zirconium dichloride,
bis(*n*-octylcyclopentadienyl)-zirconium dichloride,
bis(*n*-pentylcyclopentadienyl)-zirconium dichloride,
bis(*n*-propylcyclopentadienyl)-zirconium dichloride,
bis(trimethylsilylcyclopentadienyl)-zirconium dichloride,
bis(1,3-bis(trimethylsilyl)cyclopentadienyl)-zirconium dichloride,
bis(1-ethyl-3-methylcyclopentadienyl)-zirconium dichloride,
bis(pentamethylcyclopentadienyl)-zirconium dichloride,
bis(pentamethylcyclopentadienyl)-zirconium dimethyl,
bis(1-propyl-3-methylcyclopentadienyl)-zirconium dichloride,
bis(4,7-dimethylindenyl)-zirconium dichloride,
bis(indenyl)-zirconium dichloride,
bis(2-methylindenyl)-zirconium dichloride,
bis(2-methylindenyl)-zirconium dichloride, and
cyclopentadienylindenyl-zirconium dichloride.

22. The process as claimed in claim 19, wherein the half sandwich metallocene is selected from the group consisting of:
cyclopentadienyl-zirconium trichloride,
pentamethylcyclopentadienyl titanium trichloride,
pentamethylcyclopentadienyl-titanium Trimethoxide,
pentamethylcyclopentadienyl-titanium Trimethyl,
pentamethylcyclopentadienyl-zirconium trichloride,
tetramethylcyclopentadienyl-zirconium trichloride, and
1,2,4-trimethylcyclopentadienyl-zirconium trichloride.
23. The process as claimed in claim 19, wherein the carbon-bridged metallocene is selected from the group consisting of:

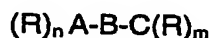
diphenylmethylidene(cyclopentadienyl)-(9-fluorenyl)-zirconium dichloride,
diphenylmethylidene(cyclopentadienyl)-(indenyl)-zirconium dichloride,
iso-propylidenebis(cyclopentadienyl)-zirconium dichloride,
iso-propylidene(cyclopentadienyl)(9-fluorenyl)-zirconium dichloride, and
iso-propylidene(3-methylcyclopentadienyl)-(9-fluorenyl)-zirconium dichloride.
ethylene-bis(9-fluorenyl)-zirconium dichloride,
meso-ethylene-bis(1-indenyl)-zirconium dichloride,
rac-ethylene-bis(1-indenyl)-zirconium dichloride,
rac-ethylene-bis(1-indenyl)-zirconium dimethyl,
rac-ethylene-bis(2-methyl-1-indenyl)-zirconium dichloride, and
rac-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)-zirconium dichloride

24. The process as claimed in claim 19, wherein the silyl-bridged metallocene is selected from the group consisting of:
dimethylsilyl-bis(cyclopentadienyl)-zirconium dichloride,
dimethylsilyl-bis(9-fluorenyl)-zirconium dichloride,
rac-dimethylsilyl-bis(1-indenyl)-zirconium dichloride,
meso-dimethylsilyl-bis(2-methylindenyl)-zirconium dichloride,
rac-dimethylsilyl-bis(2-methylindenyl)-zirconium dichloride,
rac-dimethylsilyl-bis(tetrahydroindenyl)-zirconium dichloride,
dimethylsilyl-bis(tetramethylcyclopentadienyl)-zirconium dichloride,
diphenylsilyl(cyclopentadienyl)(9-fluorenyl)-zirconium dichloride, and
diphenylsilyl-bis(indenyl)hafnium dichloride.
25. The process as claimed in any one of the preceding claims, wherein branched polymers in the form of polyolefins are formed by means of a tandem tetramerisation due to the co-catalyst and a polymerisation process due to the polymerisation catalyst.
26. The process as claimed in claim 25, the tandem tetramerisation and polymerisation process is an *in situ* catalysis process wherein tetramerisation and polymerisation takes place in the same reaction medium.
27. The process as claimed in claim 26, wherein the *in situ* catalysis process is an in-situ concurrent catalysis process.

28. The process as claimed in claim 26, wherein the *in situ* catalysis process is an *in situ* consecutive catalysis process.
29. The process as claimed in claim 26 wherein the olefin in the form of ethylene is tetramerised using the co-catalyst to produce 1-octene and the 1-octene is copolymerized *in situ* with ethylene using the polymerisation catalyst.
30. The process as claimed in claim 29 wherein the polymerisation catalyst includes a transition metal.
31. The process as claimed in any one of claims 1 to 30, which includes the step of combining the heteroatomic ligand with the transition metal compound and an activator in the presence of the polymerisation catalyst.
32. The process as claimed in claim 31, wherein the transition metal of the transition metal compound is selected from the group consisting of chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.
33. The process as claimed in claim 32, wherein the transition metal of the transition metal compound is chromium.
34. The process as claimed in any one of claims 1 to 33, wherein the transition metal compound of the co-catalyst is selected from the group consisting of an inorganic salt, an organic salt, a coordination complex and organometallic complex.
35. The process as claimed in claim 34, wherein the transition metal compound is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex, (benzene)-tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl and chromium (III) 2-ethylhexanoate.
36. The process as claimed in claim 35, wherein the transition metal compound is selected from the group consisting of chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.

37. The process as claimed in any one of claims 1 to 36, wherein the transition metal of the transition metal compound and the heteroatomic ligand are combined to provide a transition metal/ligand molar ratio from about 0.01:100 to 10 000:1.
38. The process as claimed in any one of claims 1 to 37, wherein the co-catalyst includes an activator selected from the group consisting of an organoaluminium compound, an organoboron compound, an organic salt, an inorganic acid and an inorganic salt.
39. The process as claimed in claim 38, wherein the activator is an alkylaluminumoxane.
40. The process as claimed in claim 39, wherein the transition metal of the transition metal compound of the co-catalyst and the aluminumoxane are combined in a proportion to provide an Al/transition metal molar ratio from about 1:1 to 10 000:1.
41. The process as claimed in any one of claims 1 to 40, wherein the heteroatomic ligand and the transition metal compound of the co-catalyst are combined at any temperature between -20°C and 250°C in the presence of the olefin.
42. The process as claimed in any one of claims 1 to 41, wherein the co-catalyst and polymerisation catalyst are combined in the molar ratio of 0.01:100 to 10000:1.
43. The process as claimed in any one of the preceding claims, which is carried out in an inert solvent.
44. The process of any one of the preceding claims wherein the olefin is ethylene which is contacted with the combination of catalysts at a pressure of more than 100 kPa (1 barg).
45. The process as claimed in any one of the preceding claims, wherein the polymerisation catalyst and the co-catalyst are mixed at any temperature between -20°C and 250°C in the presence of the olefin.

46. The process as claimed in any one of the proceeding claims where the process is carried out in a combination of reactors, the first reactor being a continuous stirred tank reactor and the second reactor being selected from the group consisting of a batch reactor, a continuous stirred tank reactor and a plug flow reactor.
47. A catalyst combination comprising
- (a) a polymerisation catalyst; and
 - (b) at least one co-catalyst in the form of an ethylene tetramerisation catalyst to produce 1-octene from ethylene which co-catalyst includes the combination of
 - a transition metal compound; and
 - a heteroatomic ligand described by the general formula



wherein

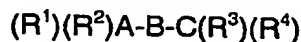
A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium and nitrogen;

B is a linking group between A and C;

the R groups are the same or different, and each R is independently selected from any homo or hetero hydrocarbyl group; and

n and m for each R is independently determined by the respective valence and oxidation state of A and C; and

provided that where the heteroatomic ligand is described by the following general formula



wherein

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen;

B is a linking group between A and C; and

R^1 , R^2 , R^3 and R^4 are independently selected from the group consisting of a hydrocarbyl group, a heterohydrocarbyl group,

a substituted hydrocarbyl group and a substituted heterohydrocarbyl group; R^1 , R^2 , R^3 and R^4 being characterised therein that either

- (i) any substituents on one or more of R^1 , R^2 , R^3 and R^4 are not electron-donating; and where R^1 , R^2 , R^3 and R^4 are independently aromatic, including heteroaromatic groups, not all the groups R^1 , R^2 , R^3 and R^4 have a substituent on the atom adjacent to the atom bound to A or C; or
- (ii) at least one of R^1 , R^2 , R^3 and R^4 is substituted with a polar substituent on a second or further atom from the atom bound to A or C and provided that any polar substituents on R^1 , R^2 , R^3 and R^4 are not on the atom adjacent to the atom bound to A or C.